On the significance of solid solution in iron (hydr)oxides for immobilisation of potentially polluting elements in ashes

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Abstract – Trace elements in ashes are frequently incorporated by the mechanism of solid solution. This means that the trace elements do not form phases in which they are major elements, but are instead distributed, one by one, in the phases formed by the major elements. A literature survey and thermodynamic calculations show that (hydr)oxides of iron and manganese probably play a major role in incorporating trace elements in less accessible forms in ash. For mine tailing containing sulphides, ashes may add the pH-buffering capacity required to avoid acidic conditions as well as supply scavengers (iron and manganese) for trace elements.

Keywords:

INTRODUCTION

Ashes from combustion and incineration of waste, recycled material or virgin biomass can be utilised for a number of purposes: forest fertilisation, geotechnical constructions, remediation of contaminated soil and treatment of tailings from mining operations. The possibilities in these regards are governed by the materials properties together with the requirements of protection of health and the environment.

Combustion and incineration are very efficient in destroying much or most of the potentially hazardous chemical substances in the waste. However, the chemical elements themselves are not destroyed, and some heavy and transition elements may form such substances that can have detrimental effects. A highly significant property in this regard is the availability of these elements to the pore water that may surround the ash particles. Most of the mechanisms for spreading of contamination as well as for uptake in human and other living organisms involve such water.

Estimations of exposures over long times are extremely difficult to make with a high precision (of e. g. ± 10 %). Consequently, large uncertainties in the exact levels are usually dealt with using conservative assumptions, e. g. that each "contamination" chemical element is present in its worst conceivable form in the chemical matrix in question.

However, overly cautious estimations may be unacceptable since they can contradict compliance with the principle of conservation which includes recycling. It is therefore imperative that estimations are also reasonably realistic. Knowledge is essential in this regard in order for

- efforts aiming at improving the protection of health and the environment to be appropriately directed, and for
- recycling to be conducted whilst maintaining adequate protection of health and the environment.

Availability to pore water is typically dealt with by

- leach testing, and by
- thermodynamic calculations

Ashes are reactive materials, and consequently, the leaching changes over time. For fly ash, this effect may imply a decrease in leaching by an order of magnitude, or more, over only a few weeks.[1] Moreover, the international literature puts forward that testing for the purpose of making predictions must be carried out in a relevant chemical environment and not in distilled water as is often the case.[2-4]

Thermodynamic calculations for the purpose of evaluating the environmental impact of the use of ashes are presently made more or less exclusively based on the assumption that all trace elements are concentrated in crystalline phases in which they are major elements. No computer codes appear to be available that allow calculations to be performed under the assumption that trace elements are incorporated in the phases formed by the major elements in the form of solid solution.

It is well known, however, from the area of geochemistry, including soil and sea sediment chemistry, that solid solutions play an extremely important role in nature in reducing the availability of many heavy and transition elements in the water phase.

OBJECTIVE

The situation described above has prompted Värmeforsk (the Swedish Thermal Engineering Research Association) to investigate the effects of solid solution with regard to trace elements in ashes.[5] The investigation comprises literature searches as well as thermodynamic calculations which include the effects of solid solubility. The literature searches include the question of why releases from historical anthropogenic constructions such as tailings from mining sometimes lead to very large releases of transition and heavy elements, whilst in other cases the environment may be surprisingly healthy. The latter is the case for the Falun copper mine which has been in operation for more than a millennium and which has had massive historical emissions and releases.[6]

The work as well as the findings have been published in a comprehensive report in Swedish.[5]

The objective of the present paper is to make the main findings in [5] available in the English language. However, reference [5] may still be of some interest to an international audience since it contains 116 references, of which only a few are mentioned in the following.

ABOUT THE INFORMATION SEARCH

The information search has comprised the following areas:

- geochemical background,
- iron (hydr)oxide phases at high and low temperatures,
- their relation to different trace elements, including zinc, lead, vanadium, nickel, cobalt, molybdenum, antimony and copper,
- tendencies for incorporation, including kinetics,
- the significance of temperature, redox potential and pH,
- presence and availability of trace elements in soil,
- manganese (hydr)oxides.

The information search has also included the following examples:

- The Falun copper mine and tailings from mining containing pyrite,
- historic releases from smelting plants,
- cesium-137 in soil,
- ashes from wood-based fuels.

References in [5] of particular interest include the following:

[7] This book contains a comprehensive description of iron oxides and hydroxides.

[8] Provides together with [9] the prerequisites for substitution and solid solution in (hydr)oxide structures

[10] Describes how thermodynamic calculations may be performed in cases of solid solubility

[11] Provides solubility versus pH data for a large number of elements and compounds. The data is compared with data for soil.

[12] The distribution of iron in the microstructure of aged ash

[13] Describes historical sites and also the stabilisation due to solid solution

[14] Description of development of acid mine drainage and its remediation
[6] The environmental history of the more than 1000 years old Falun copper mine
[15] A literature survey of the fate of caesium-137 from Chernobyl fallout in soil and ash.

GENERAL CONCLUSIONS FROM THE INFORMATION SEARCH

Hypothesis proven

Overwhelming scientific evidence in a large number of scientific publications (cf. above) show that (hydr)oxides of primarily iron, but also manganese, probably have a decisive influence for the immobilisation of trace elements in ashes by the mechanism of solid solubility.

The formation of mineral phases is governed by the major elements. The trace elements are incorporated in the crystal structures of the major elements at the atomic level. This means that the atoms of the trace elements are dispersed - one by one - in these structures. The tendency to pick up trace elements is different for different phases, and phases rich in iron as well as manganese have very strong such tendencies in comparison with other phases. This is the case for phases formed at high temperature as well as those formed through ageing (diagenesis) at low temperature.

The reason for solid solubility being such an efficient mechanism in many cases is that the entropy (a measure of "disorder") increases substantially with increasing degree of solid solubility, thus implying a substantial decrease in Gibbs' free energy.[10] Actually, it is an effect of the law in chemistry of mass action as well as of dilution. An energy term reflecting how well the minor elements fit into the structures of the major elements is also involved. Rules of thumb state that the charge of a substituting atom should preferably be ±1 relative to the atom being replaced, and that the effective diameter of the replacing atom should not differ by more than ±15 %.[8]

These mechanisms as well as their paramount significance in various natural systems have been well known in the areas of inorganic chemistry, geochemistry, and mineralogy for decades, but no case has been found in which this has been discussed in conjunction with ashes and other residues. It should also be recognised that there are several other mechanisms that may also lead to immobilisation of trace elements.

Oxides and hydroxides of iron and manganese behave as sinks for trace elements in ashes in the same manner as in soils and sediments. The main mechanism for this is solid solubility.

Although the mechanisms of solid solubility thus are very commonly occurring as well as efficient, there exists situations in which the effectiveness can be lower. They include the following:

- The solid solubility may be limited, in which case the ratio of the content of trace elements to that of reactive (hydr)oxides of iron and manganese need to be considered.
- The kinetics may be slow.
- There may be competing reactions, e. g. oxidation of pyrite by atmospheric oxygen such that the pH becomes sufficiently low in order for iron-III to go into water solution.
- Iron may form colloidal complexes such that trace elements in solid solutions may be transported with such colloides. Studies of natural analogues indicate, however, that such transport may be slow. [16]
- In the case of soil, (hydr)oxides of iron containing trace elements in solid solutions may be bonded to organic complexing agents, and in such form be transported with percolating water. This mechanism is, however, much less efficient in ashes which lack organic matter that is continually replenished and decomposed.
- The situation may be influenced by microbial activity. Such activity is low in ashes, however.

The hypothesis of solid solubility has been verified by the information search into a number of areas and by thermodynamic calculations which include the effects of solid solubility.

Most ashes contain iron and manganese in great surplus in relation to the levels of trace elements of interest. This means that the trace elements will sooner or later become incorporated in the form of solid solutions, and are not expected to appear in the form of phases in which the trace elements are major elements.

In addition, the following references provide direct evidence of the conclusions being applicable also to ashes:

- Reference [1] shows that the leaching for e. g. zinc and lead in fly ash from incineration of domestic waste and from combustion of recycled wood decreases by some order of magnitude during ageing in the presence of pore water during at least one week.
- Reference [12] that shows that trace elements in bottom ash from incineration of domestic waste is incorporated in iron-rich phases in the microstructure.

The significance of temperature

In general, and for a given crystal structure, the influence of entropy on the Gibbs' free energy decreases with decreasing temperature. It might therefore be tempting to conclude that the tendency to form solid solution would dominate at higher temperatures and be insignificant at lower temperature. This is in principle also the case for a specific phase, although in practice the decreasing mobility with decreasing temperature often causes the high temperature solid solution to remain in a meta-stable condition at lower temperature.

It is important to realise, however, that the situation may be very different for phases formed at low temperature. They typically contain substantially more of hydroxides and hydrates. This implies the following:

1 The presence of hydroxides and hydrates means that the crystal structures are much more flexible, and consequently show a much higher ability to incorporate other elements as compared to the stiff, close-packed structures that are preferentially formed at higher temperatures.

2 The lower bonding strength of the hydrogen bonds implies that the activation barriers for molecular motion become much lower, the activation higher, and thereby also the entropy. (A high activation means that there is a higher degree of occupation in the higher states; the conclusion follows from the Boltzmann distribution law).

The effect that dominates may vary from case to case. Nonetheless, it can be concluded that the solid solubility at lower temperatures is often sufficient in order for the trace elements to be incorporated in an efficient manner.

The significance of kinetics

The significance of kinetics is more difficult to discuss than that of temperature. The experience is that the kinetics are often good at furnace temperature. High temperature conditions are often locked into the structures during the rapid cooling of the fumes in a boiler. Some of the high temperature phases formed are stable or meta-stable at room temperature, and may maintain trace elements in solid solution for a long time.

Other phases are dissolved and precipitated in the form of new phases, typically with new compositions as compared to the phases from which they were formed (incongruent dissolution and precipitation). In these cases, kinetics are often favourable in that the trace elements are often liberated from the high temperature phases simultaneously with iron, and are therefore continuously incorporated into new phases in the form of solid solutions.

Trace elements and ageing

One important question is whether the phase changes that take place during the ageing will give rise to an enrichment of the trace elements in the pore water or if the pore water will become depleted with regard to such elements.

Two alternatives exist for any particular trace element:

1 The element in question is less susceptible to become incorporated in an iron-rich (alternatively manganese-rich) phase as compared to iron (alternatively manganese).
2 The element in question is more susceptible to become incorporated in an iron-rich (alternatively manganese-rich) phase as compared to iron (alternatively manganese).

Alternative (1) may apply for low abundances of the element in question in the pore water, whilst (2) may apply for high abundances. Case (2) may imply that the trace element in question becomes concentrated into the centres of the new and growing crystallites whilst the pore water becomes correspondingly depleted. This may mean that only low levels of a trace element will become liberated in a later partial dissolution that influences only the outer parts of the crystallites.

Thus, ageing typically gives rise to a more efficient incorporation of the trace elements as compared to the situation before the ageing.

Trace elements which occur in the form of chlorides

In some cases, some of the trace elements may be generated in the form of chlorides during the combustion process. Such chlorides are usually readily soluble in water, and consequently, the initial leaching is frequently high. However, there is usually a rapid hydrolysis of these ions and associated conversion into (hydr)oxide forms with a much lower solubilities. Such (hydr)oxides are subsequently likely to react with some secondarily formed (hydr)oxide of iron or manganese. One example of an element that follows such a path is zinc.[5,17-18]

THERMODYNAMIC CALCULATIONS

It was concluded in the literature survey[5] that solid solubility is a likely explanation for the experimentally observed low leach rates for aged ashes. This is most clearly obvious for zinc, for which a special investigation has been made previously[18]. However, the effect has not been included in the thermodynamic calculations found in the literature. Instead, purely stoichiometric phases have been assumed together with some adsorption parameters that can be adjusted such that a good fit with experimental data can be achieved. There is thus support for a conclusion that the effects of solid solubility are hidden in the adsorption parameters.

Thus, it is a clear oversimplification to assume that all phases are stoichiometric, and the results from such an analysis may not unveil the actual fate of the minor elements. This may be less problematic when intrapolation is to be made inside the span of parameters investigated, but may lead to large errors in cases of extrapolation outside the ranges of parameter covered by the experimental data.

The reason why non-stoichiometric phases have not been included in previous work on ashes is probably that the commercial computer codes available cannot be used for such a purpose, or can be used only with major difficulties. The study [5] has shown that the experimental data required is available in a number of cases.

Thermodynamic calculations have been conducted for the system $(Zn_xFe_{1-x})Fe_2O_4$, in which calculations have been conducted for various values for x. The end points x=0 and x=1 correspond to magnetite (Fe_3O_4) and franklinite ($ZnFe_2O_4$), respectively. Magnetite and franklinite both occur in nature. Magnetite is a common mineral while franklinite is rare.

The results show that the availability for zinc is drastically influenced by the formation of a solid solution. Moreover, the effect is larger, the lower the concentration of zinc. This concentration behaviour is quite different from that of when a trace element is assumed to be a major element in a phase of low abundance.

The results imply that when thermodynamic calculations have been made and the significance of the resulting parameters are to be interpreted, one must be aware of the fact that even an excellent fit between calculated and experimental data may not necessarily mean that the assumptions regarding the underlying mechanisms are correct. Parameters obtained from traditional thermodynamic calculations should thus not be utilised for estimations outside the areas defined by the underlying data.

Thermodynamic data from calculations that include the feature of solid solubility may, however, offer some possibilities for such extrapolation, namely for the cases in which solid solubility constitute a good fundamental description of the most important mechanisms involved. The results from the Värmeforsk (the Swedish Thermal Engineering Research Association) study [5] are directly applicable for a critical evaluation of results from thermodynamic calculations.

It is concluded that the inclusion of solid solubility would constitute a considerable improvement of the realism in thermodynamic calculations, and should therefore be developed further. It may well be that the greatest benefit of such work would be the increased realism in the evaluation of traditional thermodynamic calculations.

APPLICATIONS AND EXAMPLES

Treatment of mine tailings

Acid mine drainage may develop as a result of oxidation of sulphide minerals, primarily pyrites, by atmospheric oxygen with the aid of microorganisms. The acidity is a result of the oxidation of the sulphur in the pyrite to sulphuric acid. The pH often becomes sufficiently low to make iron-III water soluble, thus incapacitating iron that would otherwise have been an efficient scavenger for a number of heavy elements and transition elements.

Not all tailings containing sulphides form acid drainage, however. The most important factor for this is the presence of pH buffering material, e. g. limestone. In such cases, the weathering may not be self-promoting by dissolution of various species, including iron (hydr)oxides, that would otherwise protect the surfaces against further rapid attack.

The literature data found supports the conclusion that the following actions may be appropriate in order to avoid acid mine drainage:

1 To limit the access of water and atmospheric oxygen such that the rate of the neutralising action of the buffering material present exceeds that of the acid generation.

2 To add enough ash such that a sufficient pH buffering capacity is obtained.

3 To add ash - or other materials that may serve the same purpose - such that enough iron and manganese is added to incorporate trace elements in solid solution.

Ash thus has the dual role of firstly to supply sufficient pH buffering capacity to hinder iron-III to go into solution, and secondly to add sufficient iron to accommodate trace elements.

These conclusions are based on an extensive literature search[5,14], including the findings from investigations of the more than 1000 years old Falun copper mine[6].

Classification according to the directive of waste

Värmeforsk (the Swedish Thermal Engineering Research Association)[17,19-22] with some support from others [18] has previously developed a methodology for the classification of waste according to the Directive of waste[23]. For several elements, but not all, this methodology assumes the worst reasonable case regarding the forms of occurrence. However, for some elements, somewhat realistic forms have been selected. In such cases, it is essential that the choice is conservative. The present study constitutes part of the constantly ongoing work on questioning whether the conservatism is sufficient.

It is concluded that nothing has surfaced that would indicate that the previous assessments should be sharpened. Instead, the methodology is confirmed.

Acceptance for landfilling

It is obvious from the above that the leach testing carried out in conjunction with decisions on acceptance for landfilling is probably overly conservative if the tests are carried out on material that has not been aged. This has recently been confirmed in a study [1] which showed that the leaching of e. g. zinc and lead decreases by more than an order of magnitude already after a few weeks of ageing of the ash in the presence of free pore water.

The standard[3] referred to in the acceptance criteria for landfilling [2] states that it is applicable only for such materials that do not react with the leachant (which is water). If, nonetheless, an accredited test laboratory performs the test on fresh ash, then the laboratory is obligated to make a note of the deviation from the standard in their protocol. One of the present authors have read a great number of such protocols, but in no case has there been any such notation.

Insignificant risk in conjunction with geotechnical constructions

Geotechnical use of ashes is legally acceptable in Sweden and other EU countries only if the impact on health and the environment is shown to be insignificant. In practice, this is dealt with at two levels: the generic and the site specific levels. At least in the generic case[24], the assessment is based on concentrations of trace elements of interest in combination with conservative assessments on the chemical speciation.

Since such trace elements in ash are frequently strongly incorporated in the phases formed by the more or less insoluble major elements, such assessments may well be more cautious than actually justified from a conservation and recycling point of view.

Therefore, it may be preferable in many cases to make site and material specific analyses, e. g. according to Reference [24]. The properties of the material to be used can be determined by the following:

1 Empirically by leaching of the ash material after realistic ageing, and

2 theoretically by thermodynamic modelling using computer codes that allow calculations that include solid solutions.

CONCLUSIONS

The main conclusions are as follows:

Trace elements in ash do not usually form phases in which they are major elements.

Trace elements in ash are frequently incorporated in (hydr)oxides of iron as well as manganese in the form of solid solution.

The atoms are dispersed one by one and are essentially inaccessible.

In conjunction with tailings from mining of sulphide ores, ash can supply iron and manganese for scavenging action (if needed).

At the same time, ash can supply the pH buffer capacity needed for such action to take place.

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